ARMY RESEARCH LABORATORY

Investigating a Drop-on-Demand Microdispenser for Standardized Sample Preparation

by Ellen L. Holthoff, Mikella E. Hankus,
Keeley Q. Tober, and Paul M. Pellegrino

ARL-TR-5726   **September 2011**

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Sensors and Electron Devices Directorate, ARL

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14. ABSTRACT

The existing collection of reference sample preparation methods presents a range of variability and reproducibility concerns, making it increasingly difficult to assess chemical detection technologies, especially in regard to techniques that are spatially dependent. To overcome these challenges, we are examining the optimization, characterization, and calibration of microdroplets from a drop-on-demand (DOD) microdispenser that is ideal for the preparation of energetic reference materials. Current research focuses on the development of a sample preparation protocol for explosive materials testing based on DOD technology. The results presented here demonstrate the operational factors that influence droplet dispensing of specific materials (e.g., energetic and interferent). Ultraviolet-visible (UV-Vis) absorption spectroscopy and Raman spectroscopy are used to investigate droplet and sample uniformity and reproducibility (typical calibration goodness of fit R^2 values of 0.991, relative standard deviation or RSD $\leq 5\%$). DOD results are compared to samples prepared using a drop-and-dry method.

15. SUBJECT TERMS

Drop-on-demand, injet printer, microdrop, energetics

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1. Introduction

The detection and identification of trace explosive residues on surfaces is a priority for the military and homeland defense applications, and first responders. Technology evaluation of systems based on optical detection techniques that allow for ranged sensing is complicated by spatial dependencies and a lack of a reliable means to generate calibrated reference samples containing the explosive materials. Reference materials and methods are needed to establish benchmarks for hazard detection system development, verification of system performance in the field, and technology comparisons between systems. Furthermore, an assortment of explosive reference materials is needed to allow for flexibility to react to the diverse and ever-changing range of threats encountered. A variety of techniques that offer temporary alternatives have been employed, including drop-and-dry (dropcasting) and spray deposition methods; however, there is often uneven sample coverage (i.e., coffee ring effect) and material waste. Using drop-on-demand (DOD) inkjet printing technology to produce test materials is an attractive approach to meet the requirements for sample standardization. Samples produced using piezoelectric DOD inkjet printing have eliminated the coffee ring effect, resulting in a more homogeneous sample coverage (*1*) (the coffee ring effect and an array of microdroplets are illustrated in figure 1(a) and (b), respectively).
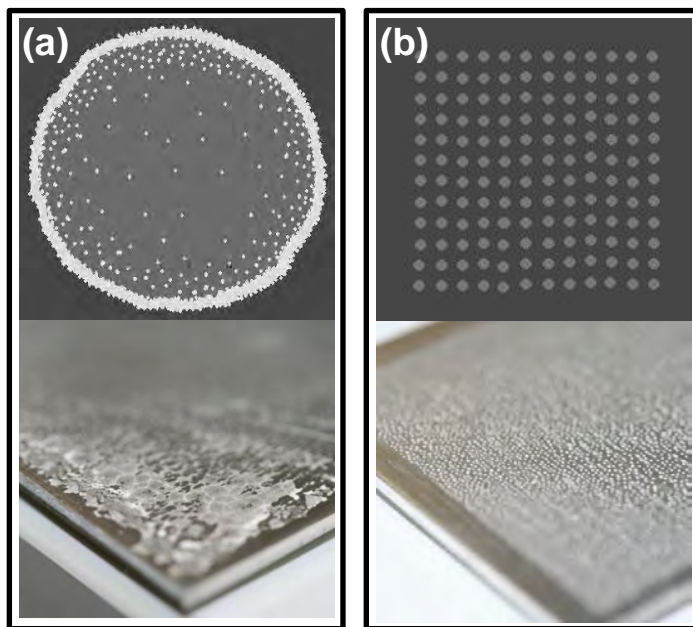

Figure 1. (a) Graphic and photograph of drop and dry sample deposition demonstrates uneven dispersion and the coffee ring effect. (b) Graphic and photograph of an array of microdroplets demonstrates a more even sample dispersion when sample is dispensed with a DOD microdispenser.

Piezoelectric DOD inkjet printing is an efficient approach for non-contact deposition of microdrops of solutions onto a surface (2). This technique is compatible with various liquids, providing precise control over material deposition. Additionally, a range of deposited material concentrations can be achieved by varying the number and spacing of microdrops printed. As a non-contact printing process, the inkjet fluid cannot be contaminated by the substrate or contamination on the substrate, and the fluid can be easily dispensed into wells or other substrate features (3). DOD technology has been successfully used in a variety of applications, including the printing of photodiodes, polymer and protein arrays, and in electronics manufacturing (4–7). These applications benefit from the wide range of liquids that can be dosed, the small volume to be handled, the accuracy of drop placement, and the quantitative volume delivery. The reproducibility of optimized DOD systems has been reported to be better than 1% relative standard deviation (RSD) from measurement to measurement (within-day) and better than 2% RSD for day-to-day measurements of dispensed volumes (8, 9).

Currently, we are using a DOD printing platform for the preparation of numerous types of samples to be used in a field test for the assessment of an explosives detection system. Here, we report the development and feasibility of this sample preparation method to produce both energetic and interferent test materials. Microdrop mass was determined and validated by absorbance measurements using an ultraviolet-visible (UV-Vis) spectrophotometer. These measurements allowed for a simple and inexpensive system calibration to verify the mass of various target materials deposited with each drop. In this report, we will also discuss the uniformity and reproducibility of samples prepared using the DOD inkjet printer, and compare these findings to those obtained from samples prepared using a drop-and-dry method.

2. Experimental

2.1 Reagents and Materials

Target Analyte Stock Solutions. Ammonium nitrate (AN), methanol, distilled water, acetonitrile, sugar, urea, and potassium chlorate were obtained from Sigma-Aldrich. 1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-tetrazocine (HMX), 2,4,6-trinitrotoluene (TNT), and pentaerythritol tetranitrate (PETN) were obtained from Cerilliant. All inkjet printer stock solutions were prepared in a solution of methanol (MeOH) and water (v/v 2:1), acetonitrile, or water, depending on solubililty. All stock solutions were sonicated for 30 min prior to use to ensure homogeneity.

Substrate Materials. Inkjet-produced test materials were prepared on bare aluminum coupons purchased from OnlineMetals.com (Aluminum 5052-H32 bare sheet, 2 in. x 4 in.) or painted test panels purchased from ACT Test Panels (55911 TRU ALM 03X03X025 cut only no hole unpolished coil coated gray: 1370AC301 clear: RK8148 GEN 4 AC55891, 55891 TRU ALM

03X03X025 cut only no hole unpolished coil coated gray: 1370AB921 clear: RK8148 GEN 4 AC, and 55946 BASELL TRC779X 2.5X3.5X090 cut only; type: TPO not hole topcoat: 509ADI018 super white). Upon receipt, the bare aluminum substrate coupons were thoroughly washed using an acetone solution to completely remove any residual grease or contamination from the factory. Following the acetone cleaning, the coupons were dried and an ethanol-containing wipe was used to remove any residual contamination. Inkjet-produced materials used to assess microdrop and sample uniformity and reproducibility were prepared on aluminum-coated glass substrates obtained from Evaporated Metal Films Corporation. Substrate dimensions were 1 in × 3 in.

All chemicals and materials were used as received unless otherwise noted. To minimize the impact of humidity, test materials were placed in an oven (30–40 ºC) after jetting to ensure all solvent had completely evaporated. After complete drying, materials produced for validation and process reproducibility experiments in our laboratory were vacuum-sealed in custom-made Gel-Pak® containers and stored in an oven (30–40 ºC) prior to additional analysis.

2.2   Inkjet Printing

Test materials were produced using a JetLab® 4 (MicroFab Technologies) tabletop printing platform. The system is shown in figure 2(a). The JetLab® 4 is a DOD inkjet printing system with drop ejection drive electronics (JetDrive™ III), pressure control, a drop visualization system, and precision *X*, *Y*, *Z* motion control. The dispensing device (print head assembly, MJ-AL-01-060) consists of a glass capillary tube, with a 60 μm diameter orifice coupled to a piezoelectric element. Photographs of the dispensing device encasement and the print head assembly are given in figures 2(b) and 2(c), respectively.   Voltage pulses (20–25 V; rise time 1 μs; dwell time 28–32 μs; fall time 1 μs) applied to the piezo result in pressure fluctuations around the capillary. These pressure oscillations propagate through the printing fluid in the tube, resulting in ejection of a microdrop. Drops are visualized using synchronized strobe illumination and a charged coupled device (CCD) camera (figure 3). Determining optimal jetting parameters is a trial-and-error process. Stable droplet ejection is achieved by visually observing expelled microdrops and adjusting voltage pulse parameters and capillary fluid backfill pressure. Conditions that provide the highest drop velocity without satellite droplet formation are desired. Printing was performed at a frequency of 250 Hz with a droplet velocity of ~2 m/s. Drop diameter was estimated to be ~60 μm, based on the capillary orifice diameter. Using Aphelion software supplied by MicroFab Technologies, images of drops generated were analyzed and subjected to strict quality control, ensuring droplet diameters and, hence, volumes produced were consistent throughout analyte sample preparation. Thus, the Aphelion software was used as an additional validation method for the concentration or amount of analyte dispensed per droplet.
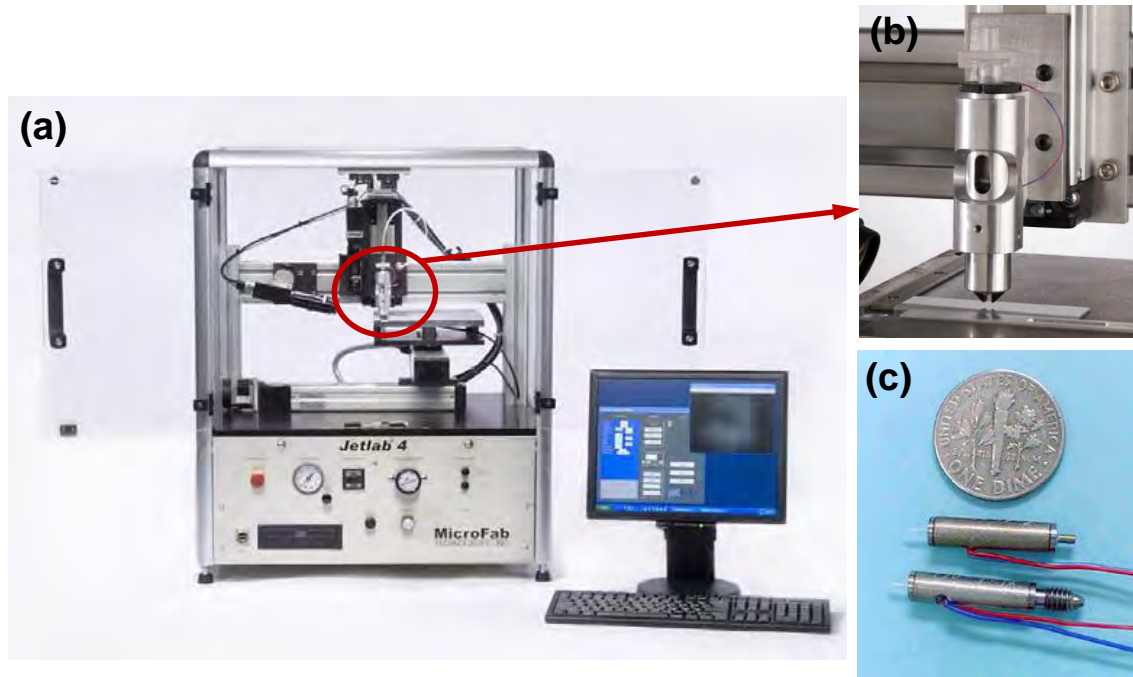
Figure 2. Photographs (*10*) of (a) JetLab® 4 DOD inkjet printing platform, (b) dispensing device and ink solution encasement, and (c) print head assembly.
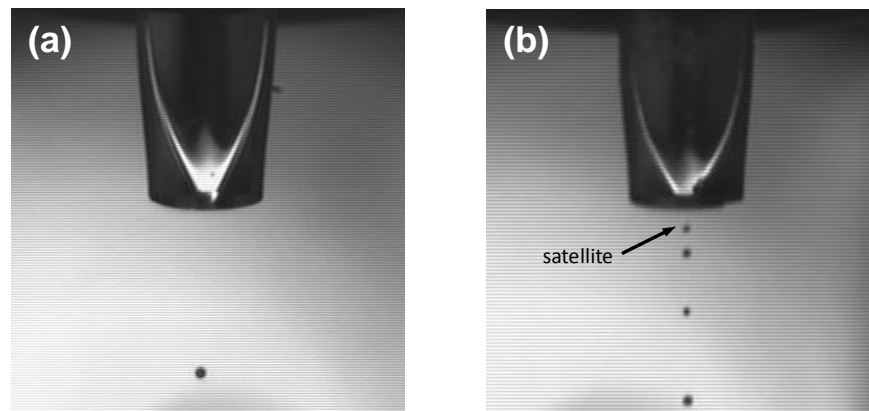
Figure 3. Drop generation from JetLab® 4 DOD inkjet printer. Stable droplet ejection (a) is achieved by adjusting voltage and pressure parameters. Satellite drop formation (b) is not desired and can often be eliminated by decreasing the voltage.

For clarification, definitions and parameters optimized are listed as follows:

- Dwell time: the time amount when the piezo wave form changes shape when a drive voltage is applied for a given amount of time.

- Optimal drop: a droplet typically equal in size to the dispensing orifice being used, does not have satellites, and falls at an optimum velocity consistently.

- Satellite: secondary droplets, following the optimal droplet, typically observed to be smaller in volume than the optimal droplet. Satellites deposited add to a total concentration error and can affect droplet spacing uniformity.

- Optimum velocity: typically around 1–2 m/s.

- Voltage: voltage applied to the piezoelectric device.

During printing, a single substrate was placed on the sample stage. The print head remained fixed at a specified height while the stage moved to print a specified pattern. A rectangular array, which covers a rectangular area with rows of equidistant points, was pre-programmed based on the substrate size and desired sample concentration. An array pattern was chosen for the purpose of creating the effect of a homogeneous coating for optical interrogation. Depending on the desired concentration per unit area (e.g., $\mu g/cm^2$), the total number of drops needed to achieve the desired concentration in that area was calculated based on the mass of a single microdrop (see Supporting Information). Based on the number of total drops needed, the array spacing and drops needed per line can be calculated. These values are easily adjusted depending on concentration. Arrays were printed using the print on-the-fly mode. In this mode, the stage moves continuously as a single microdrop is dispensed at each array element. Print on-the-fly mode improves sample throughput.

2.3 Drop and Dry

Test materials were produced using the drop-and-dry method. An aliquot of solution was dispensed (no more than 200 µL at a time, with drying) onto a substrate and spread across the substrate surface with a pipette tip as the solution evaporated, leaving only sample material residue spread across the substrate surface.

2.4 UV-Vis Absorption Spectroscopy

UV-Vis absorption spectroscopy measurements were collected using a Shimadzu® UV-3600 UV-Vis spectrophotometer. Calibration curves were constructed by measuring standard solutions (of known sample concentrations) containing various pre-determined energetic and interferent compounds. The evaluated analytes were: AN, potassium chlorate, HMX, TNT, RDX, PETN, urea, and sugar. The analyte of interest was dissolved in the appropriate solvent and then diluted to various concentrations. Absorbance was measured using quartz cuvettes (1 cm path length) in a dual beam UV-Vis. One cuvette was filled with 3 mL of analyte solution (sample), and the other was filled with 3 mL of pure solvent (blank, H_2O or acetonitrile). Wavelength scans from 190–400 nm were used to measure the absorbance of the various target materials at known concentrations. The analytes of interest had absorption features in this wavelength region.

2.5 Raman Spectroscopy

Raman data was recorded using a Renishaw inVia Reflex Raman microscope equipped with a near-infrared diode laser excitation source ($\lambda = 785$ nm). The light from the diode was focused onto the sample at the microscope stage through a 20x (individual drop measurements) or 100x (intra-drop measurements) objective. Neutral density filters were used, resulting in reduction of the maximum available laser power to 5 mW. Samples at the microscope stage were positioned remotely with a joystick using an encoded, motorized *XYZ* translation stage (0.1 μm step size) controlled by a Prior Scientific ProScan II controller. WiRE 3.2 software, operating on a bench top PC, was used for instrument control and data collection. Before all measurements, the instrument was wavelength calibrated using an internal silicon standard.

Duplicate samples were prepared for each study, and five separate spectral acquisitions were obtained for each sample. Each Raman spectrum was collected over a range from 600 cm^{-1}– 1200 cm^{-1}—with a 30.00 s exposure time and a spectral resolution better than 1 cm^{-1}—and is the result of one accumulation.

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3. Results and Discussion

We report microdroplet optimization results for a dispensing device having a 60 μm orifice with analyte samples in conjunction with acetonitrile, MeOH:H_2O, and H_2O solvents. We also discuss the performance for the microdrop mass calibration method described, as applied to various inkjet stock solutions. This includes the repeatability and standard uncertainties of the measurements. Potential biases arising from variations in operational conditions are considered. We also report the reproducibility of the DOD inkjet printer for producing AN test materials and the uniformity of these samples, as compared to the drop and dry sample preparation method.

3.1 Microdroplet Optimization Results

Prior to analyte deposition onto a substrate surface, it was important to completely understand the DOD instrument settings, and the influence of the dispensing device orifice size and the inkjet printing solvent used. Many variables can impact the drop; therefore, optimized parameters are needed to achieve the best drop at a sufficient velocity. *Controlling the physical properties (e.g., size, volume) of the dispensed microdrops and the ability to do so is very important, as these parameters will ultimately affect droplet variation and reproducibility.* Desired drop velocity is between 1 and 2 m/s. In all cases, it was found that in order to maintain a consistent drop with a suitable velocity, several variables needed to be changed, including the dwell time and voltage applied to the dispensing device.

Using a 60 μm diameter dispensing device, acetonitrile proved to be a challenging solvent for obtaining and maintaining an optimal drop. The parameters shown in table 1 were uniquely

capable of producing a good satellite-free drop. In order to maintain a consistent drop, the dwell time needed to be set between 31 and 34 µs. As the dwell time was increased, the voltage could be set between 17 and 22 V. We found that by increasing the dwell time and voltage, the velocity of the drop increased (shown in figure 4(a)). While maintaining a consistent drop, the velocity did not change at voltages greater than 18 V. The highest velocity found was 1.11 m/s.

Table 1. Parameters for an optimal drop using acetonitrile and a 2:1 MeOH:H_2O ratio solution with a 60 µm dispensing device orifice.

Solvent	Tip Size	Dwell Time	Voltage	Velocity
Acetonitrile	60	31	17	0.888
		34	19	1.11
MeOH:H_2O	60	28	20	1.11
		28	21	1.332
		30	23	1.554
		31	28	1.998
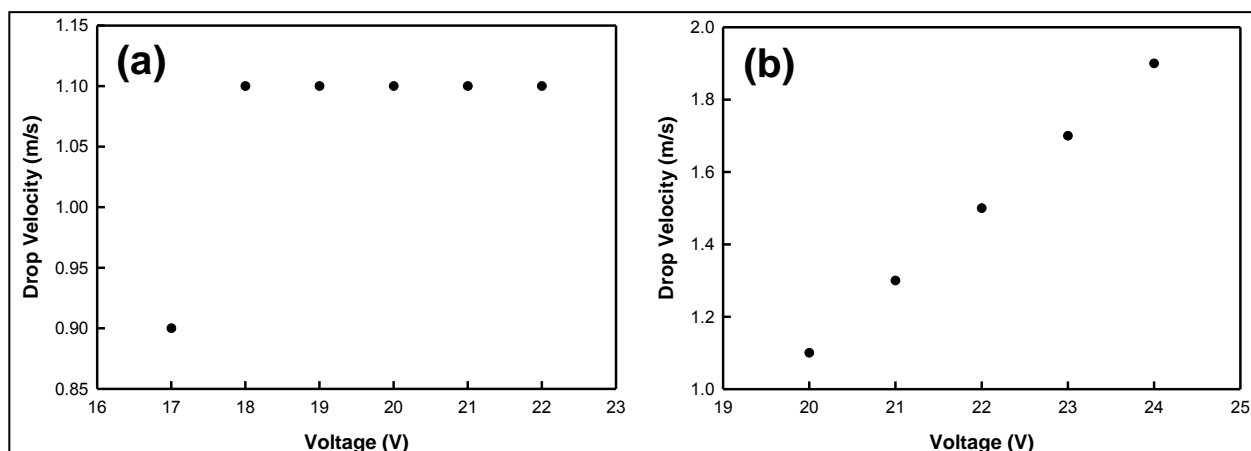
Figure 4. Using a 60 µm dispensing device, changes in drop velocity at different voltages for (a) acetonitrile and (b) 2:1 MeOH:H_2O ratio solution are shown.

When we used a 60 µm tip, the MeOH:H_2O solution proved to be an easy solvent with which to work, because many settings could be used to obtain a good drop (parameters shown in table 1). In order to maintain a consistent drop, the dwell time needed to be set between 28 and 31 µs. With the dwell time set within those limits, the voltage could be set between 20 and 28 V. We found that by maintaining the same dwell time but increasing the voltage, the velocity of the drop increased (shown in figure 4(b)). Increasing the voltage above 24 V resulted in a loss of drop consistency. Therefore, setting the dwell time and velocity at 31 µs and 24 V, respectively, gives the best drop with the optimum velocity.

3.2 Microdroplet Mass Determination

To determine the microdroplet mass for each material of interest, a calibration curve was constructed using known concentrations of analytes and absorbance spectral peak areas (shown in figure 5(a)). Calibration curves were used to prepare linear regressions from which the microdroplet mass and standard error could be calculated using the equation of the line and goodness of fit value (R^2 value). The equation of the line was of the form $y = mx + b$, where y is the peak area, m is the slope, x is the concentration, and b is the y intercept. Example absorbance spectra and the corresponding calibration curves for AN, TNT, and HMX are shown
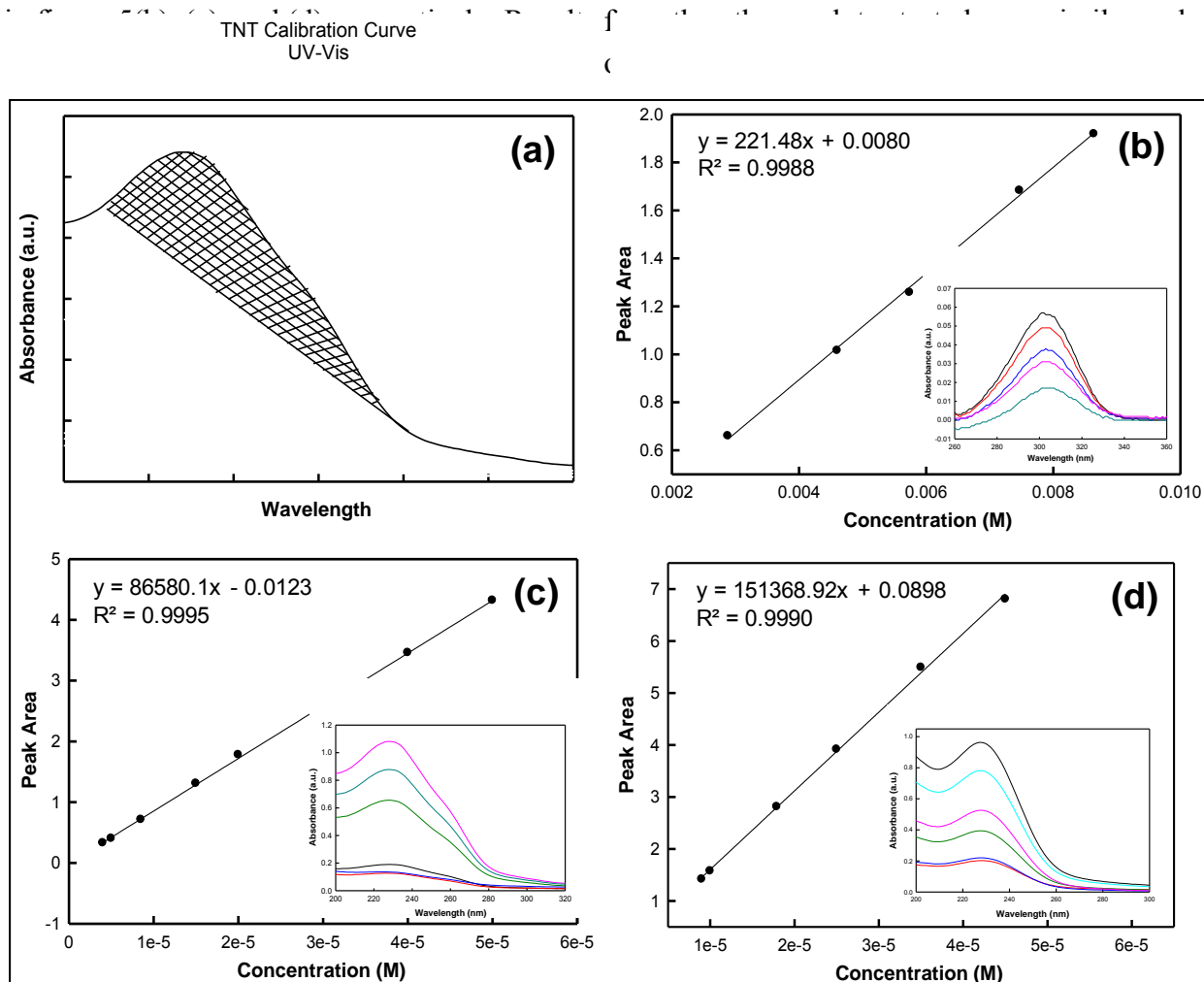
Figure 5. (a) Example absorbance spectrum illustrating peak area used to construct UV-Vis calibration curves.
(b) AN calibration curve and R^2 value from one UV-Vis data set at various analyte concentrations.
(c) TNT calibration curve and R^2 value from one UV-Vis data set at various analyte concentrations.
(d) HMX calibration curve and R^2 value from one UV-Vis data set at various analyte concentrations.

By determining the mass of material dispensed per droplet, test materials containing a range of sample concentrations can be successfully produced. The mass per drop of each analyte of interest was determined by dispensing known numbers of drops into a Petri dish containing a

known amount of solvent. Spectral peak areas for these droplets in solution were determined from the UV-Vis absorbance spectra. These y values were then substituted into the respective calibration curve equation (y = mx + b) to determine solution concentration. This methodology was repeated at least three times and resulted in excellent typical RSD values of 5%.

3.3 Sample Reproducibility and Uniformity

AN sample reproducibility and uniformity was determined using Raman spectroscopy. Spectra of the deposited, individual AN microdrops were acquired over the Raman shift range from 600 cm^{-1}—1200 cm^{-1}. A typical AN Raman spectrum collected over this wavelength range is provided in figure 6. This spectral region is interesting since it contains features representative of Raman-active components present in AN. The spectra are dominated by features centered near 715 cm^{-1} and 1044.6 cm^{-1}. For sample-to-sample and within-sample comparisons, the peak height of the main Raman spectral band at ~1044.6 cm^{-1} (the symmetric stretch mode of the NO_3^-) was used.
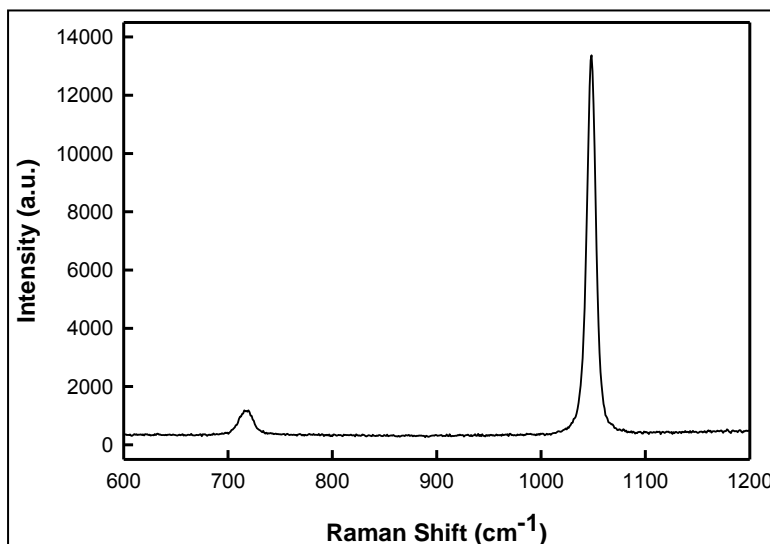
Figure 6. Raman spectrum recorded for AN on an aluminum coated glass substrate.

Peak heights were determined by taking the difference between the peak intensity maximum and an average baseline for each spectrum. The results of the Raman measurements taken for three 50 μg/cm^2 AN samples prepared using the DOD inkjet printing platform are displayed in figure 7. Ten spectra were recorded at different locations (i.e., drops) throughout each sample. The average RSD for the sample-to-sample reproducibility was 19%. This variation is apparent in the spectra, which illustrates the significant intensity differences from drop to drop, most noticeably in samples 1 and 3. These deviations are in part due to differing physical properties of the dispensed microdrops. Droplet visualization during the printing of these samples confirmed the sporadic appearance of satellite drops throughout the process. The appearance of satellites was most evident and abundant during the printing of sample 3. The drop-to-drop

variation within each of the three samples was 7%, 20%, and 26%. Drop morphology, or the
focus of the micro̶̶n.
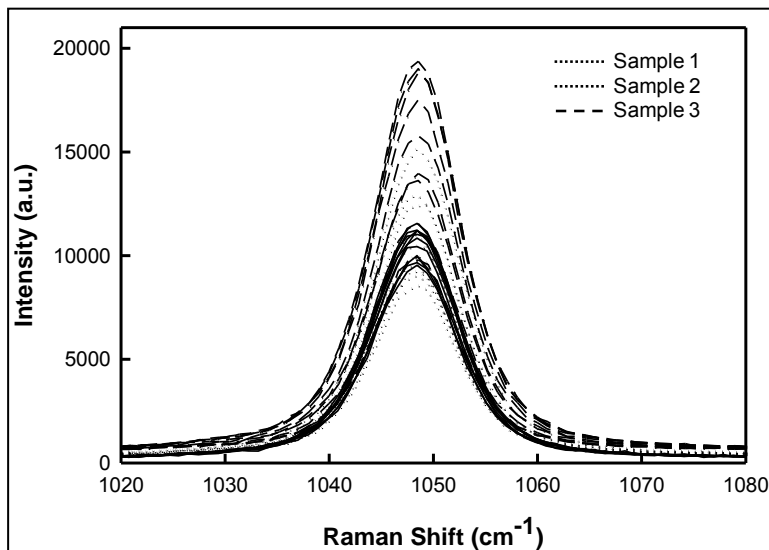
Figure 7. Raman spectra collected for three different AN samples prepared
using the JetLab[®] 4 DOD inkjet printer. Spectra were recorded at
10 different spots (drops) on each sample.

Although an effort was made to collect each Raman spectrum at a similar region within each
drop, additional variability arises across the drop, itself. This is illustrated in figure 8. Using a
100x objective on the Raman microscope allowed for interrogation at multiple positions within a
single drop. The Raman intensity varied based on the location within the residue. This is due to
the distribution of the material throughout the drop. The highest intensity was observed at point
3 and the lowest at   ıcter of the drop.
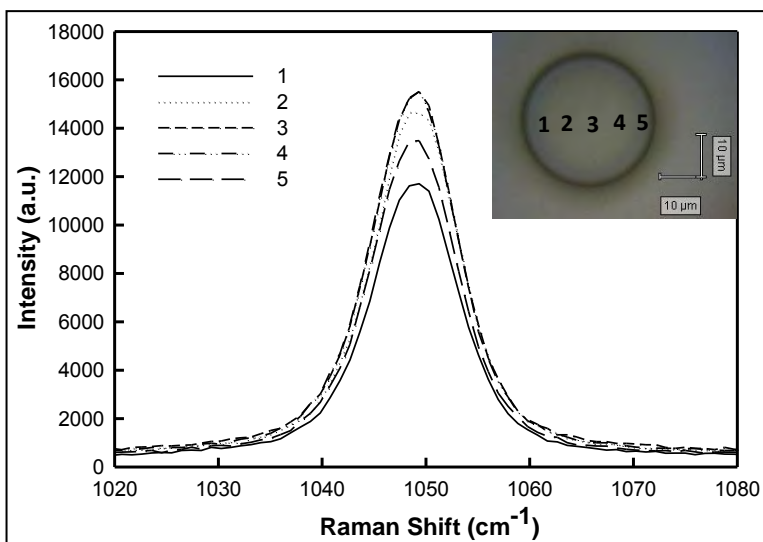

Figure 8. Raman spectra collected at different points across a single drop
(inset) in a sample prepared using the JetLab[®] 4 DOD inkjet printer.

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For comparison purposes, an AN sample was prepared using the described drop-and-dry method, and a series of Raman spectra were collected at several different locations throughout the sample. The data is given in figure 9, along with microscope images of each investigated area. Not only do the intensities of the spectra vary significantly, the microscope images show very different concentrations of AN in each location. Based on these results, a RSD value of almost 100% was calculated for this sample, which is at least four times greater than the calculated variation for the samples prepared using the DOD inkjet printer. Given that the RSD for the DOD samples was determined based on drop-to-drop variation within a sample, we expect that the RSD for an area of drops would be ≤20%, and the variance between the drop-and-dry and DOD techniques would be more significant. A comparison of these sample preparation methods and the uniformity achieved with each can be easily illustrated using scanning electron microscope (SEM) images and photographs, which are provided in figure 10. Clumping of AN on the surface of the substrates is evident in figure 10(c) and (d), while a more even material dispersion is apparent in figure 10(a) and (b). Unlike other sample preparation methods that often result in the coffee ring effect, for which most of the material is concentrated along the edges, samples prepared using the DOD inkjet printer have an excellent uniform material
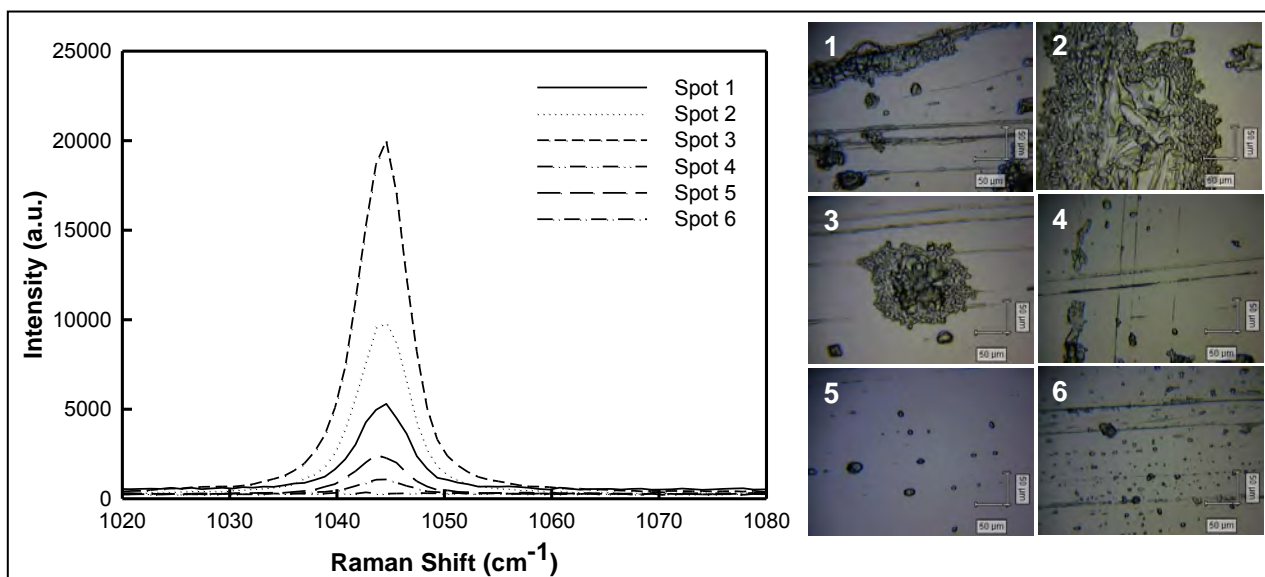

Figure 9. Raman spectra collected at different points across a sample prepared using the drop and dry method.
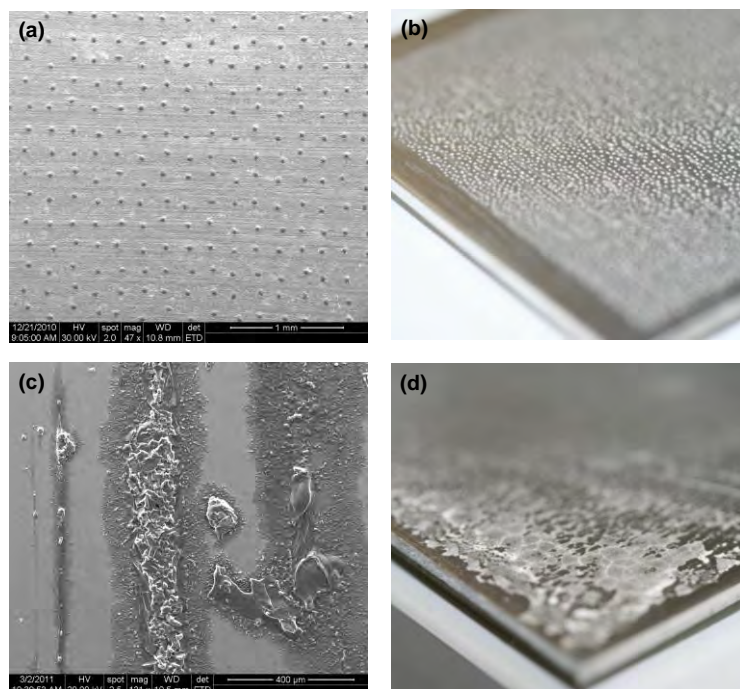
Figure 10. SEM images of samples (at different magnifications) prepared using the (a) JetLab® 4 DOD inkjet printer and (c) drop and dry method. (b) and (d) are photographs of these samples, respectively.

4.   Conclusion

We have investigated a sample preparation protocol that produces uniform samples to be used for utility assessments of emerging detection technologies. We developed a method for determining the mass of droplets ejected from a DOD inkjet printing platform that allows for system calibration and the preparation of specific sample material mass loadings. Optimization of microdroplet formation provides microdispensing with specific drop placement and pattern printing capabilities. Overall, samples prepared using a DOD inkjet printer are more uniform as compared to those prepared using a drop and dry method. Continued improvements to the inkjet system and sample preparation procedures will further decrease RSD values for the microdrop samples. Based on these findings, we can confidently conclude that using the DOD system in combination with our analysis and validation technique is ideal for the fabrication of reference energetic samples, and should be considered a predominant and universal innovative industry standard.

5. References

1. Holthoff, E. L.; Hankus, M. E.; Pellegrino, P. M. Investigating a Drop-on-Demand Microdispenser for Standardized Sample Preparation. *Proc. SPIE - Int. Soc. Opt. Eng.* **2011**, *8018*, 80181F–80190F.

2. Lee, E. R. *Microdrop Generation (Nano- and Microscience, Engineering, Technology and Medicine)*. CRC Press: Boca Raton, FL, 2003.

3. MicroFab Technologies, I. Background on inkjet technology *Technical Notes No. 99-01* [Online], 1999. www.microfab.com/equipment/technotes/technote99-01.pdf.

4. Miettinen, J.; Kaija, K.; Mantysalo, M.; Mansikkamaki, P.; Kuchiki, M.; Tsubouchi, M.; Ronkka, R.; Hashizume, K.; Kamigori, A. Molded Substrates for Inkjet Printed Modules. *Ieee Transactions on Components and Packaging Technologies* **2009**, *32* (2), 293–301.

5. Singh, B. K.; Hillier, A. C. Multicolor Surface Plasmon Resonance Imaging of Ink Jet-printed Protein Microarrays. *Analytical Chemistry* **2007**, *79* (14), 5124–5132.

6. Xia, J.; Qu, D.; Yang, H. N.; Chen, J. J.; Zhu, W. L. Self Assembly Polymer Microlens Array for Integral Imaging. *Displays* **2010**, *31* (4-5), 186–190.

7. Yang, Y.; Omi, S.; Goto, R.; Yahiro, M.; Era, M.; Watanabe, H.; Oki, Y. Wavelength Sensitive Photodiodes in the Visible Based on J-type Aggregated Films Patterned by Inkjet Method. *Organic Electronics* **2010**, *12* (3), 405–410.

8. Englmann, M.; Fekete, A.; Gebefugi, I.; Schmitt-Kopplin, P. The Dosage of Small Volumes for Chromatographic Quantifications Using a Drop-on-demand Dispenser System. *Anal. Bioanal. Chem.* **2007**, *388*, 1109–1116.

9. Windsor, E.; Najarro, M.; Bloom, A.; Benner, B.; Fletcher, R.; Lareau, R.; Gillen, G. Application of Inkjet Printing Technology to Produce Test Materials of 1,3,5-trinitro-1,3,5-triazcyclohexane for Trace Explosive Analysis. *Anal. Chem.* **2010**, *82*, 8519–8524.

10. MicroFab Technologies, Inc. www.microfab.com.

Supporting Information

Sample Microdrop Mass Calculation

For TNT calibration curve, linear fit equation is $y = 86580.1x - 0.0123$. Based on the peak area for an unknown printed sample (2 arrays printed into 6 mL of water, 2.80×10^4 drops per array), the predicted concentration from the calibration curve is 1.04×10^{-5} M.

$$1.048 \times 10^{-5} \frac{mol}{L} \times 0.006\, L = 6.2 \times 10^{-8}\, mol$$

$$6.2 \times 10^{-8}\, mol \times 227.1 \frac{g}{mol} = 1.408 \times 10^{-5}\, g\ TNT$$

$$\frac{1.408 \times 10^{-5}\, g}{56000\ drops} = 2.51 \times 10^{-10} \frac{grams\ TNT}{drop} = 2.51 \times 10^{-4} \frac{\mu g\ TNT}{drop}$$

Microdrop mass averages (table 2) and RSD values (figure 11) were determined by averaging at least five successive additions of a single array to the 6 mL volume.

Table 2. Inkjet target analyte solution concentrations and corresponding calibrated drop mass.

Material	Solution Conc. (M)	Drop Mass (ug)
Ammonium Nitrate	1.20	1.15E-02
Ammonium Nitrate	0.050	3.79E-04
Urea	0.98	6.44E-03
Sugar	1.00	1.98E-02
RDX	0.045	4.30E-04
HMX	0.027	5.01E-04
TNT	0.022	2.65E-04
PETN	0.011	4.18E-04
Potassium Chlorate	0.39	5.61E-03

PET
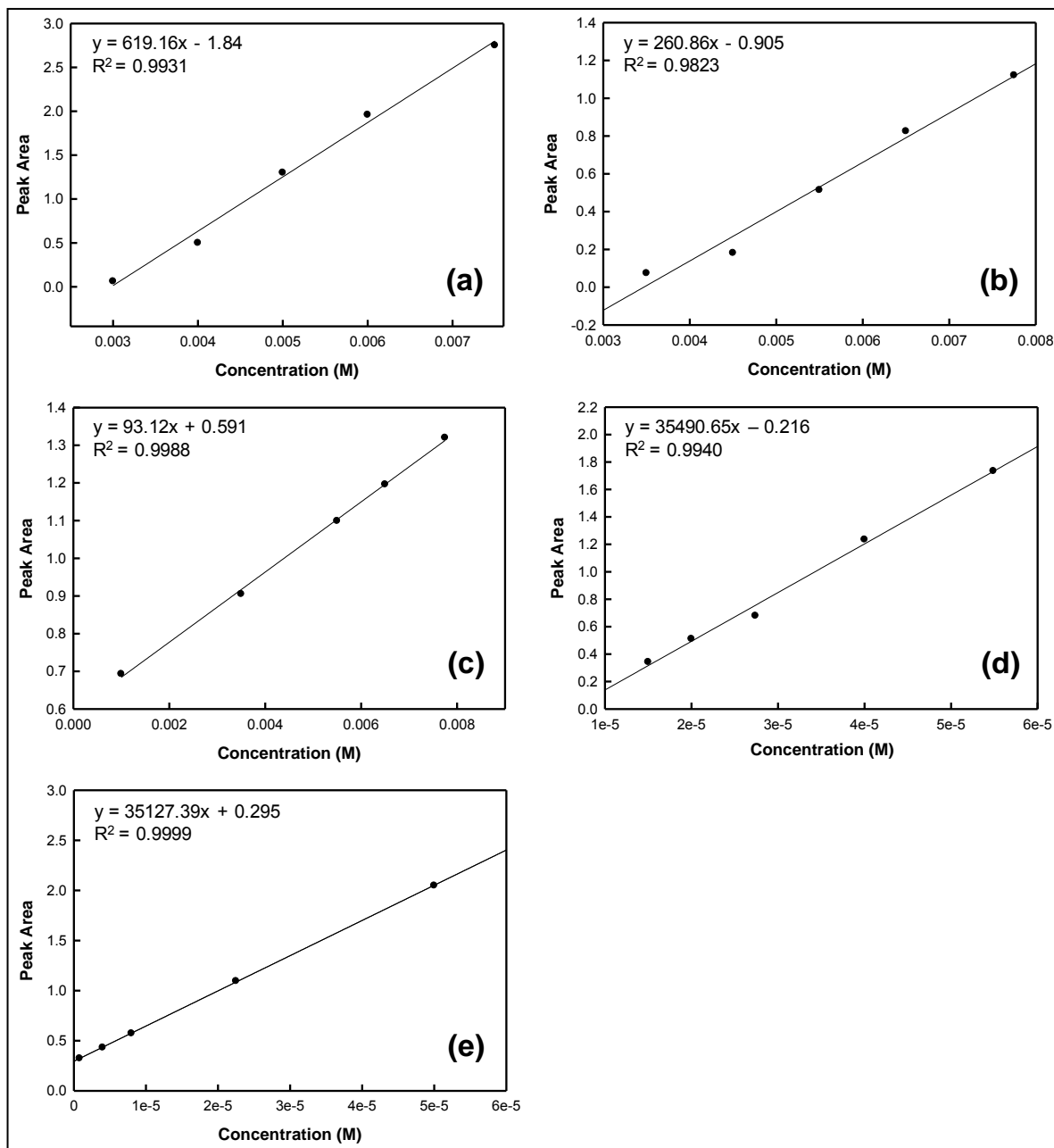
Figure 11. (a) Urea calibration curve and R^2 value from one UV-Vis data set at various analyte concentrations. (b) Potassium chlorate calibration curve and R^2 value from one UV-Vis data set at various concentrations. (c) Sugar calibration curve and R^2 value from one UV-Vis data set at various concentrations. (d) PETN calibration curve and R^2 value from one UV-Vis data set at various concentrations. (e) RDX calibration curve and R^2 value from one UV-Vis data set at various concentrations.

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1 HC 1 ELEC	ALAKAS DEFENSE SYSTEMS TAMPA OFFICE ATTN E DOTTERY (1 ELEC, 1 HC) 7935 114TH AVE N. STE 1100 LARGO FL 337733 dottery@alakai.us
13 HCS 8 ELECS 3 CDS	US ARMY RSRCH LAB ATTN IMNE ALC HRR MAIL & RECORDS MGMT ATTN RDRL CIO LL TECHL LIB ATTN RDRL CIO MT TECHL PUB ATTN RDRL SEE G WOOD (1 ELEC) ATTN RDRL SEE L BLISS (1 ELEC, 1 HC)

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D STRATIS-CULLUM (1 ELEC)
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(3 HCS, 1 ELEC)
ATTN RDRL SEE O M HANKUS
(3 HCS, 1 ELEC)
ATTN RDRL SEE O N FELL (1 ELEC)
ATTN RDRL SEE O P PELLEGRINO (3 HCS, 3 CDS, 1 ELEC)
ATTN RDRL SEE P GILLESPIE (1 ELEC)
ADELPHI MD 20783-1197

TOTAL: 43 (19 HCS, 3 CDS, 21 ELEC)

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